Information

CHEMISTRY 146/246 - KINETICS AND MECHANISM

COURSE OUTLINE

I. Aims of Mechanistic Organic Chemistry
II. Kinetics: reaction order, some simple cases, experimental techniques, practical kinetics, steady-state kinetics, reactions involving prior equilibria
III. Inferences from Reaction Order: limitations of kinetics, following kinetics by more than one technique
IV. Theoretical Considerations: Principle of Microscopic Reversibility, linear free-energy relations, selectivity principle, Hammond's principle
V. Acid and Base Catalysis, Brønsted catalysis law, More O'Ferrall-Jencks Diagrams
VI. Entropy and Enthalpy of Activation
VII. Medium Effects
VIII. Isotope Effects: primary, secondary, solvent
IX. Substituent Effects
X. Steric Effects and Conformational Effects
XI. Inferences from Unusual Reactivity
XII. Product Studies: orientation, stereochemistry, regiochemistry, labeling experiments, crossover experiments
XIII. Demonstration of Existence of Intermediates: trapping experiments, blocking experiments, labeling experiments, detection or isolation of intermediates
XIV. Mechanistic Inference by Analogy

RECOMMENDED TEXTS (NONE TRULY SUITABLE)

Organic emphasis: Felix A. Carroll, "Perspectives on Structure and Mechanism in Organic Chemistry", 2ed, Wiley (2010).
Inorganic emphasis: J. H. Espenson, "Chemical Kinetics and Reaction Mechanisms", McGraw-Hill, 2ed (1995).
Biochemistry emphasis: W. P. Jencks, "Catalysis in Chemistry and Enzymology" Dover (1969).
Advanced: E. V. Anslyn & D. A. Dougherty, "Modern Physical Organic Chemistry", University Science Books (2006)
Reference books: March, Lowry & Richardson, Carey & Sundberg

CHEMISTRY 146/246 Course Description

DESCRIPTION

Chemistry 146/246 is an advanced organic chemistry course dealing with a quantitative
approach to solution kinetics and organic reaction mechanisms. The aim is to present the various
methods for determining reaction mechanisms. Lectures will cover theory, practical kinetics, and

examples of applications of the methods.

Chemistry 146/246 is intended for students with a good preparation in organic chemistry. It is offered only every two or three years! All first- and second-year graduate students in organic chemistry are expected to register. Graduate students in inorganic chemistry, biochemistry, and physical chemistry will also benefit from the course. Qualified undergraduates (recommended 3.0 GPA in Chemistry 140ABC) are encouraged

CHEMISTRY 246 PAPER

Lectures are the same for both 146 and 246, but a further requirement of Chemistry 246 is to write and submit a paper that reviews a recent research publication in the area of kinetics and mechanism.

Students must choose a recent (2011 or later) research paper (not a review) that presents solution kinetics, along with an additional experimental technique such as substituent effects, stereochemistry, isotopes, buffer catalysis, solvent effects, or activation parameters (DeltaH‡, DeltaS‡) that provide information about reaction mechanism. Avoid papers that emphasize molecular structure, equilibria, analytical methods, computations, or gas-phase reactions. The journals *J. Am. Chem. Soc., J. Phys. Org. Chem., J. Org. Chem., Org. Biomol. Chem., Angew. Chem., Chem. Eur. J., Tetrahedro*n, and *Org. Lett*. contain the most suitable papers, so search their Table of Contents for title words "kinetics", "rates", "catalysis", "reactivity", or "activation barrier". Alternatively, search at *www.webofknowledge.com*. Post the reference to your paper in the discussion file Papers Chosen at the course website (*http://ted.ucsd.edu*), and consult those postings so that you do not choose the same paper as someone else has chosen.

Read both the paper and any Supporting Information carefully, imagining that you were assigned to carry out this project and then to summarize your results. Pay attention to the question that is being addressed, how it was approached, what the results were, and what they mean. You will need to read many of the references that were cited. To write your paper, start by describing the Methods, in more detail than provided concisely in the original paper. Then present the Results, with tables and structures as needed. Explain the most important Conclusions, and then write an Introduction that presents the question that was addressed (and goes at the beginning even though it

is written last). On the first page include the title of the paper, the authors, the source, and a brief
Abstract.

Everything that you write must be your own words. Except for the reference citations and
the data (in the form of tables and figures as necessary), nothing can be copied from the original
paper, including individual sentences. UCSD's prohibition of plagiarism is outlined within the
section on Integrity of Scholarship online at
senate.ucsd.edu/manual/Appendices/Appendix2.pdf.
Submit your paper by e-mail to cperrin@ucsd.edu. It should be attached as a Microsoft
Word file (but not .docx), with embedded structures in ChemDraw (or with additional ChemDraw
files) and with a .pdf copy. Use your name as the title of the files. Use MSWord to eliminate errors
in spelling and grammar. The deadline is 5 PM, Friday, May 30. You will be judged by the clarity
of your presentation.